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Battelle
Columbus Laboratories

Report

FINAL PROGRESS REPORT
(March 1979 through September 1979)

on

ULTRAPURE GLASS OPTICAL WAVEGUIDE
DEVELOPMENT IN MICROGRAVITY
BY THE SOL-GEL PROCESS
(JPL CONTRACT 955361)

to

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

February 22, 1980

by

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INTRODUCTION

The melting of glass in a terrestrial environment involves an obstacle to maintaining low purity levels due to contamination by container walls, a problem which can be alleviated by containerless melting in the space environment. The ultimate objective of the present research program is to take advantage of the containerless melting of glasses in space for the preparation of ultrapure homogeneous glass for optical waveguides. However, the homogenization of the glass using conventional raw materials is normally achieved on earth either by the gravity induced convection currents or by the mechanical stirring of the melt. Because of the absence of gravity induced convection currents, the homogenization of glass using conventional raw materials will be difficult in the space environment.

Multicomponent, homogeneous, noncrystalline oxide gels can be prepared by the sol-gel process and these gels are promising starting materials for melting glasses in the space environment. The sol-gel process referred to here is based on the polymerization reaction of alkoxysilane with other metal alkoxy compounds or suitable metal salts.[1,2] Many of the alkoxy silanes or other metal alkoxides are liquids and thus can be purified by distillation.[3] The use of gels offers several advantages such as

high purity and lower melting times and temperatures. Hence, the present
research program aims at utilization of the sol-gel process for the
preparation of multicomponent ultrapure glass batches for subsequent
containerless melting of the batches in space to prepare glass blanks
for optical waveguides.

Prior to "space rea?'~ess", however, several critical control
points must be carefully evaluated on earth. Hence, the present ground
based program plan comprises two major phases.

Phase I involves the following activities:

- Selection of the best multicomponent glass system
  suitable for optical waveguides
- Choice of compositions in a particular system
- Preparation of gels in the chosen multicomponent
  system (with reagent grade chemicals) by different
  procedures
- Thermal treatment of gels for removal of volatiles
  and water
- Characterization of gels
- Melting of gels prepared by different procedures
- Characterization of the resulting glasses in terms
  of properties relevant to optical waveguide
  applications.

Phase 2, to be initiated in a follow-on effort, plans to concentrate
on the following activities:

- Preparation of ultrapure gels by using ultrapure chemicals
  and a class 100 clean room
- Melting of ultrapure gel pellets using both a container
  and containerless melting
- Characterization of glasses in terms of trace level
  transition metal impurities and absorptive losses.

The present report deals with initial activities of Phase 1 of
the program.

SUMMARY

The results of the initial activities of the present program can be summarized as follows:

- An alkali-borosilicate system has been chosen for the present work. The choice was made after considering various material characteristics, such as absorption losses, physical properties, processing parameters, and availability of ultrapure chemicals

- The factors influencing the absorption losses of the glasses in the $Na_2O-B_2O_3-SiO_2$ system have been analyzed critically. At present, one composition has been selected for the development of the gel preparation procedure. However, several compositions which are expected to give low loss glass fibers have been suggested for future studies

- Several gel preparation procedures based on two different approaches have been developed. The first approach consists of the reaction of all reactants (mostly alkoxides) in nonaqueous solvents, and subsequent gelation on adding a limited amount of water. The second approach involves the initial partial hydrolysis of tetraethyl orthosilicate by the addition of water and a catalyst before the addition of other constituents

- The removal of organic groups from the gels by low temperature thermal treatments (<500 C) have been investigated in terms of gel preparation, and thermal treatment procedures. Results show that the gel preparation procedure has an influence on the removal of organic groups. The presence of more active water during gelation or after gelation has a beneficial effect on the removal of organic groups

- No crystallinity of the gels develop after thermal treatment up to 500 C

- Infrared spectroscopic studies of the gels prepared by
  the different procedures show that the spectra of
  the gels prepared by the different procedures are not
  identical. It appears that there exists some finer
  structural difference in the gels prepared by different
  procedures. It is speculated that this difference could
  be due to the difference in the polymeric structures of
  the gels originated by the different preparation pro-
  cedures.
- The elimination of carbon from the glass during the
  melting of gels containing organic residues has been
  investigated. The removal of carbon is a function of
  time and temperature. The increase of temperature from
  1000 C to 1200 C reduces the time of melting from 5 hours
  to 1 hour for getting a colorless bubble-free glass.

EXPERIMENTAL WORK AND RESULTS

The experimental work done in this initial period of the program has been divided into the following activities:

- Choice of glass system
- Choice of composition
- Preparation of gels
- Thermal treatment of gels
- Characterization of gels
  - Crystallinity
  - Molecular structure
- Melting of gels.

Choice of Glass System

The most important requirement for selecting a glass system for optical communication is its transparency in certain wavelength regions. However, the flexibility of fabrication of glass fibers of a particular geometry (e.g., graded index with high numerical aperture) is also of considerable importance from the manufacturing viewpoint. A simple fabrication process leads to reduced cost when large quantities of fiber are made.

Although the high silica fibers made by the CVD technique had an early success because they can be prepared free from impurities, the possibility remains that some multicomponent glass systems might be ultimately preferred for the following reasons:[4,5,6]

- They can be melted and drawn into fiber at temperatures much lower than that required for high SiO_2 compositions.
- They are available in a wide variety of compositions with a broad range of refractive index and thermal expansion properties. Hence, there exists a great flexibility in the choice of optical, mechanical and chemical properties.

- Transparency of multicomponent glasses may be less
  sensitive to some contaminants than that of pure SiO_2

The choice of a multicomponent system depends primarily on the
desired characteristics of the optical attenuation in the fiber. The
optical attenuation in fiber waveguides is due to the sum of the bulk
material attenuation (i.e., optical loss in bulk glass) and attenuation
due to fabrication.

The bulk material attenuation, which is the characteristic of the
material is comprised of two types

- Absorption loss
- Scattering loss.

Hence, the absorption and the scattering characteristics of a
glass should be critically analyzed to achieve highly transparent glasses
for optical waveguides.

The absorption loss is comprised of two parts, intrinsic ab-
sorption and absorption due to impurities. The contribution of intrinsic
absorption to the total absorption is needed to assess the fundamental
lower limit for any particular material. However, there is considerable
disagreement about the relative importance of the intrinsic absorption
because it is difficult to conclusively assign measured optical absorption
to an intrinsic or an impurity effect. The picture becomes more complicated
because the transition metal impurities exist in more than one valence
state in the glass, each valence state contributing absorption bands of
different intensity, shape, and position. The relative proportions of the
different valence states, and thus the optical loss coefficients of metals
depend on the glass system, composition, and the conditions of melting and
firing of the glass.

The scattering loss in glass can be of two types

- Intrinsic scattering loss
- Scattering loss due to defects or inhomogenities
  developed during material fabrication.

Intrinsic scattering loss is due to the density and composition
fluctuations in glass. The intrinsic scattering loss due to frozen-in

density fluctuations depends on the glass transition temperature, T_g, but this should be less with glasses having lower T_g.

It may be concluded, therefore, that the material characteristics that are required for the reduction of intrinsic optical attenuation in glass are as follows

- A large energy gap to minimize absorption in the red and near infrared due to the tail of the ultraviolet absorption band.
- A low glass transition temperature to minimize scattering due to density fluctuations.
- Components with well matched dielectric properties to minimize scattering due to compositional fluctuations.

In the present study, the following three systems have been examined in terms of material properties and fabrication procedures:

- Alkali Borosilicate
- Alkali Aluminosilicate
- Alkali Germanosilicate.

Table 1 gives a brief analysis of these systems in terms of the following parameters:

- Absorption losses
- Scattering losses
- Refractive index
- Suitability for sol-gel preparation
- Availability of ultrapure starting chemicals
- Processing parameters.

It is evident from the information available in these systems[4,5,7,8] that both alkali borosilicate and alkali aluminosilicates are prospective candidates. The advantages of soda aluminasilicates are: low intrinsic scattering losses, the removal of OH groups should be easier. There is a lack of knowledge about the influence of the composition on the absorption coefficient of iron in this system. The absorption coefficient of iron might be higher in this system and thus, it might be difficult to reduce

TABLE 1. MATERIAL CHARACTERISTICS OF MULTICOMPONENT SYSTEMS

Material Characteristics	Alkali Borosilicate	Alkali Aluminosilicate	Alkali Germanosilicate
Intrinsic Absorption	No information on the intrinsic absorption loss is available in literature; glasses having absorption losses as low as 5 dB/km have been made.	Estimated intrinsic absorption loss in certain compositions should be as low as silica.	No information is available on the ternary system, but the preparation of low loss glasses in the GeO_2-SiO_2 has been reported. The presence of alkali should not cause problem.
Absorption Due to Impurities	Absorption loss depends considerably on the compositions and melting conditions even when the total impurities content is same.	No information is available, but likely the loss should depend basically on the total amount of impurities, compositions should have an insignificant effect.	It should depend on the total impurity content; most likely, compositions would have little effect.
Intrinsic Scattering Loss	Presence of liq-liq immiscibility zone cause high scattering loss in certain areas; but compositions away from the immiscibility zone should have very low scattering loss.	Scattering loss of most compositions should be very low; in one composition scattering losses less than 1/4 of that of pure silica have been observed.	No information is available in ternary system. Theoretically, low scattering values are expected.
Physical Properties	Refractive index and thermal expansion coefficient can be changed slowly by changing compositions.	Refractive index can be changed slowly by changing the composition.	The refractive index can be changed with the change of composition.
Suitability to Gel Preparation	Preparation of glasses via the sol-gel technique can be developed.	Preparation of glasses via the sol-gel route can be developed.	In principle, it is possible to prepare via the sol-gel route.
Processing Parameters	Temperatures of processing of certain compositions are lower than those in other two systems. Low glass transition temperatures.	Processing temperatures are higher than those of glasses in alkali borosilicate system. Glass transition temperature should be higher.	Processing temperatures should be lower than those of alkali aluminosilicate system, but should be higher than those of alkali borosilicate system.
Availability of Raw Materials	Ultrapure starting chemicals such as H_3BO_3, Na_2CO_3 are commercially available. Tetraethoxysilane can be purified	Al-alkoxide might be purified by distillation; however, the highest purity level which could be attained is not known.	$Ge(OC_2H_5)_4$ is a liquid, and might be purified by distillation.

the loss due to iron, which is the most abundant impurity. Moreover, most
of the compositions in this system require higher melting temperatures.
Thus, silica crucibles as such cannot be used. However, the H. F. induction
melting could be an alternative. The spectroscopic studies of transition
metal ions in $Na_2O-B_2O_3$ and Na_2O-SiO_2 systems[9] suggest that the absorption
coefficient of iron is expected to be markedly low in $Na_2O-B_2O_3$ system,
whereas the coefficients of the other elements would remain the same in
both systems. According to the work of Milberg[10] et al, the spectro-
scopic behavior of transition elements in the alkali borosilicate system
should be similar to that in alkali borate. It should be pointed out
that iron is the most abundant impurity in all pure chemicals, and the
iron content of airborne particulate matter is also high. Hence, any
approach which will reduce the absorption loss due to the iron is worth
considering. Hence, the alkali borosilicate system has this important
feature of controlling the absorption loss due to the presence of iron.
Moreover, several glass compositions in the alkali borosilicate system
can be melted at lower temperatures, and the system offers flexibility
in the choice of optical and physico-chemical properties. However, there
are some restrictions for working in this system. The existence of a
liquid-liquid immiscibility zone restricts the choice of compositions in
the whole ternary system.[11] The removal of hydroxyl groups from glass
melts having high B_2O_3 content is an extremely difficult experimental task.
Nevertheless, the recent works[4,5,6] on the development of low loss
(~5 dB/Km) optical glass fibers. Hence, the alkali borosilicate system
has been selected for the present work.

Choice of Compositions

The following characteristic features of this glass system in
relation to the absorption loss have been considered before selecting the
suitable compositions.

- Liquid-liquid immiscibility
- Effect of Na_2O content
- Effect of B_2O_3 content
- Effect of the redox state of the glass
- Hydroxyl content.

Liquid-Liquid Immiscibility

The presence of a liquid-liquid immiscibility zone in the $Na_2O-B_2O_3-SiO_2$ system restricts the choice of composition in all areas of the glass-forming region in this system. The projection of the immiscibility surface at different temperatures is shown in Figure 1. The compositions must be chosen outside the metastable liquid-liquid immiscibility zone. However, there exists a large glass-forming zone outside the liquid-liquid immiscibility zone. Thus, several compositions having various physico-chemical properties (such as refractive index and thermal expansion coefficients) can be selected from the glass forming zone outside the metastable liquid-liquid immiscibility zone.

Effect of Na_2O Content

The absorption coefficient due to iron, falls as the percentage of soda in the soda borosilicate glass is reduced[4]. The decrease of the soda content, however, does not affect the copper attenuation. Decreasing the soda content also causes attenuation coefficient due to cobalt and nickel to fall. Thus, the total loss of the glass can be reduced by reducing the soda content. The extinction coefficient of Fe^{+2} reduces with decrease of Na_2O content in glasses of constant $SiO_2:B_2O_3$ ratio. This has been demonstrated by Beales, et al[4] and is illustrated in Figure 2, but the decrease in Na_2O content brings the composition toward the metastable immiscibility zone.
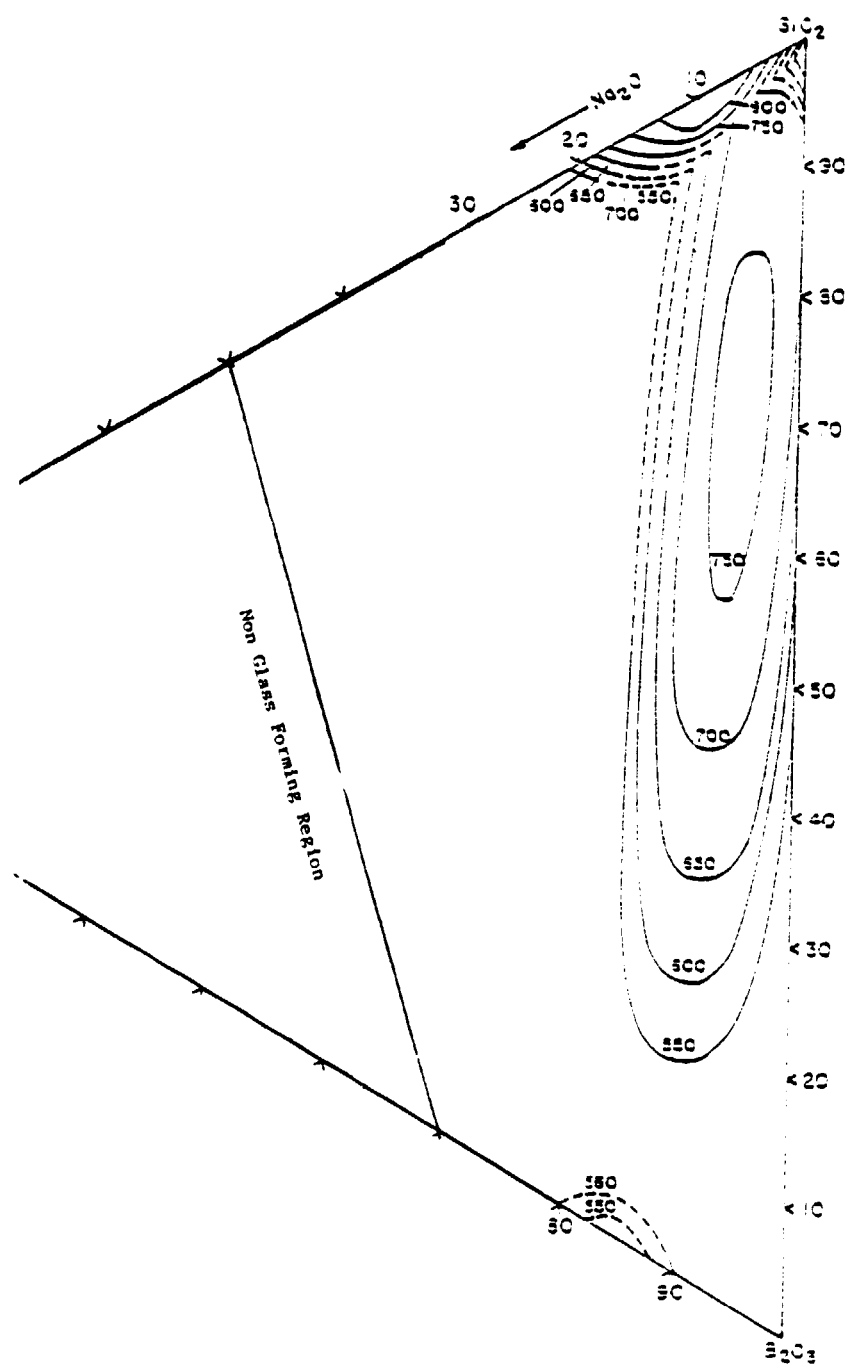
FIGURE 1. $Na_2O-B_2O_3-SiO_2$ TERNARY DIAGRAM SHOWING
THE PROJECTION OF THE IMMISCIBILITY
SURFACE AT DIFFERENT TEMPERATURES (11)
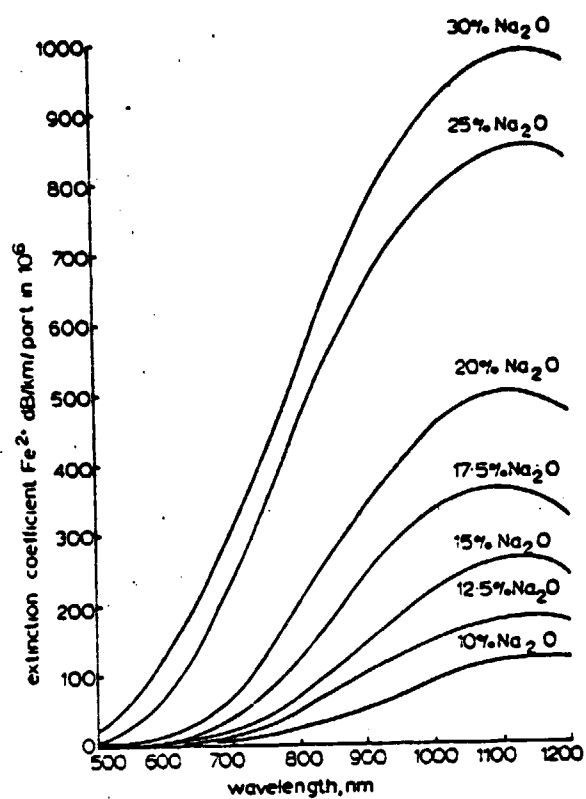
FIGURE 2. VARIATION OF EXTINCTION COEFFICIENT
OF Fe^{2+} WITH GLASS COMPOSITION[4]

Effect of B_2O_3 Content

Absorption loss decreases with the increase of B_2O_3 content. This is because of the fact that the absorption loss due to iron and copper is dependent on the boric oxide content of the glass.[4] The basic reason for this phenomenon might be related with the boron coordination number in the structure of glass and its influence on the transition metal valence states.

Effect of the Redox State of the Glass

The iron absorption loss in a wavelength region of our interest is due to iron in ferrous (Fe^{+2}) state, and the copper absorption loss is due to Cu^{+2} (oxidized) state. Thus, a particular redox state of the glass should be attained which will bring the total absorption coefficient to a minimum, and those factors that influence the redox state of the glass are important. These factors are:[4,12]

- Oxygen potential of melting atmosphere
- Melting temperature
- Minor reducing or oxidizing additives such as As_2O_3, Sb_2O_3, etc.

Oxygen Potential of Melting Atmosphere. The effect of oxidizing and reducing conditions on the attenuation coefficients of Fe and Cu studied by Beales, et al[4]. The results reported by Beales, et al[4,12] are shown in Figure 3. The results indicate that the attenuation coefficient of Cu decreased tenfold on bubbling with CO/CO_2 gas mixtures, but such treatment caused a large increase in the Fe attenuation coefficient. According to these workers[4,12], if the levels of Fe and Cu are known in a pure melt, the total loss due to Fe and Cu may be minimized by using an intermediate redox state. It is reported[4,12] that high losses are obtained under strongly oxidizing and reducing conditions with a minimum
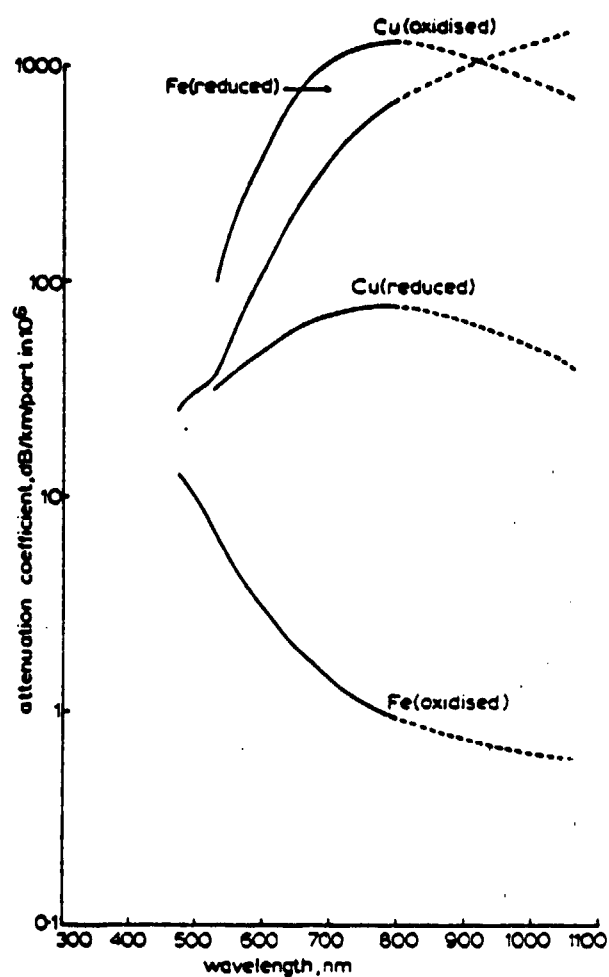
FIGURE 3.   ABSORPTION LOSSES OF Fe AND Cu
            DOPED SODIUM BOROSILICATE
            GLASSES SHOWING OXIDIZED AND
            REDUCED STATES[4]

loss at an intermediate state. The position and level of the minimum
depend on the ratio of Fe to Cu in the glasses, and on their relative
extinction coefficients.

Melting Temperature. The dependence of absorption loss on
temperature is almost certainly due to the effect of temperature on the
redox state of the glass. It is repeated[4] that the copper absorption
loss falls as the temperature of melting is raised, and the iron absorp-
tion loss increases as the temperature of melting is raised. The melting
temperature is thus an important parameter in producing glasses with
minimum absorption loss.

Minor Additives, such as AS_2O_3, Sb_2O_3. A very small additive
of AS_2O_3 acts as a buffer against changes in the redox state so that
the melt can be held at a high temperature for a considerable period
of time without major alteration of the redox state.

Hydroxyl Content

The solubility of water vapor in silicate or borate melts (under
equilibrium conditions) is dependent on the composition. The effect has
been explained on the basis of the acid-base concept of the melts. It has
been expected that the solubility of water vapor should increase both with
increasing acidity and with increasing basicity, and thus it should be
minimum at a neutral point. This has been investigated[13] with simple
binary systems like alkali borate system. No systematic work has been
reported in the alkali borosilicate system. However, it may be concluded
that the melts of high acidity with high B_2O_3 content should possess a
high affinity for water. Consequently, it would be more difficult to
remove hydroxyl groups with increase of B_2O_3 content at a certain Na_2O
content.

Hydroxyl groups in a silicate glass have a fundamental stretching
vibration at 2800 mm, and overtones at 1400, 960 and 740 μm. A typical
absorption curve of sodium borosilicate glass is shown in Figure 4.
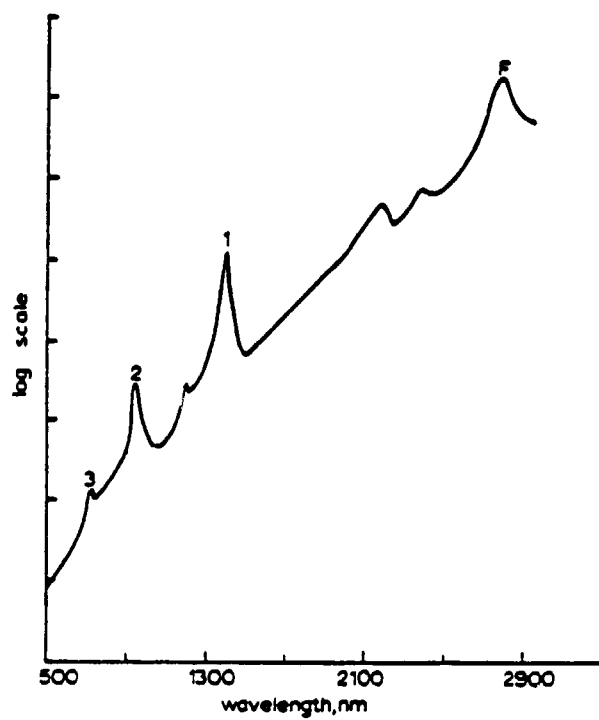
FIGURE 4. HYDROXYL OVERTONE AND COMBINATION
BANDS. SODIUM BOROSILICATE GLASS[4]

In regard to the molar absorptivity, the information available in the literature shows that the molar absorptivity of hydroxyl groups in silicate glasses has a range of values from 43 for fused silica to 18.5 lit $mol^{-1}cm^{-1}$ for soda lime glass.[14] Recently, the average molar absorptivity of OH groups in alakli-borosilicate glass of a particular composition (SiO_2 45, B_2O_3 35, Na_2O 20 mole percent) has been reported[15] as 30 lit $mol^{-1}cm^{-1}$. This appears to be of the same order of magnitude as 38 lit $mol^{-1}cm^{-1}$ for a borate glass containing 20 percent Na_2O. It is hard to predict the effect of the composition in a wide range. The reduction of OH content of the glass can be affected by taking the following measures[4]:

- Removal of surface water by baking the initial powders under vacuum at 250 C

- Bubbling of dired gas N_2 or O_2 (dew point -60 C) through the glass melt.

Conclusion

It may be concluded that the selection of the suitable compositions for getting low loss glasses depends on several factors which should be evaluated by experimental investigations. However, the objective of the initial work in this program is to develop the gel preparation procedures and evaluate and characterize the gels prepared by the different procedures. Hence, the study of the gel preparation has been done with the following composition (in weight percent):

$$SiO_2\text{-}60, \quad B_2O_3\text{-}15, \quad Na_2O\text{-}25.$$

This composition lies far away from the metastable liquid-liquid immiscibility zone. When the gel preparation process and the relation of gel structure to the glass structure are understood to some extent, a series of compositions suitable for getting low loss glasses will be investigated. The effect of increasing the B_2O_3 content could be investigated with the following compositions:

SiO_2	B_2O_3	Na_2O (weight percent)
50	25	25
25	50	25

According to some previous work [4] the above compositions give low loss glasses when processed under the optimum experimental conditions.

Preparation of Gels

The development of the gel preparation procedures has been considered in terms of several factors which are important for fulfilling the objectives of the present research program. The following factors have been considered.

- Chemical nature of the starting compounds and the purity attainable with the starting compounds
- Homogeneity of the multicomponent solution and the gelling process
- Removal of volatile organic or inorganic compounds by thermal treatment
- Crystallinity of gels.

Starting Compounds

The following starting compounds can be used as sources of different oxides in the different procedures. The compounds marked with an asterisk have been used in the present work.

Oxide	Source
SiO_2	Tetraethyl orthosilicate*
	Tetraethyl orthosilicate hydrolysate
	Tetramethoxy silane
B_2O_3	Boric Acid*
	Trimethyl Borate*

Oxide	Source
Na_2O	Sodium Carbonate[*]
	Sodium Nitrate[*]
	Sodium Acetate[*]
	Sodium Methylate[*]

It should be noted that the compounds which can easily be available in ultrapure conditions are:

Tetraethyl Silicate Hydrolysate

Boric Acid

Na_2CO_3 and $NaNO_3$.

Tetraethyl orthosilicate monomer is not available in ultrapure condition, however, ultrapure tetraethyl orthosilicate hydrolysate which is obtained by the partial hydrolyses of the tetraethyl orthosilicate can be available on the market. Other chemicals in the above list are not available on the market but they can be, in principle, purified to ultrapure conditions. Because the initial objective was oriented more towards the understanding of the gelling process and the characterization of gels, the availability of the chemicals in ultrapure conditions was not of main concern.

The status of the ultrapurity of each starting compound is stated below:

H_3BO_3
Na_2CO_3 — Now available commercially as ultrapure materials for optical fiber application

Tetraethyl orthosilicate hydrolysate (obtained by the partial hydrolysis of tetraethyl orthosilicate) — Capable of being purified to ultrapure conditions

Sodium Nitrate
Sodium Acetate — Capable of being obtained in ultrapure conditions

Sodium Methylate — It has not yet been tried experimentally

Triemethyl Borate — Capable of being purified to ultrapure

Homogeneity of The Solution and The Gelling Process

Because the homogeneity of gel in terms of cation distribution is an important objective of the present work, the preparation procedures have been critically judged in terms of homogeneity. Thus, the stability of the solution on addition of different constituents and the homogeneity that could be achieved were considered.

The homogeneity of the solution and the stability of the solution are influenced by various process parameters such as the nature of reactants, the pH of the medium, the concentration of the reactants, the presence of minor additives. A qualitative assessment of the above factors have been made.

Removal of Organic Groups

The removal of residual organic groups from the gel by low temperature (<500 C) thermal treatments is a complex process and appears to be related to the gel preparation procedures. The primary concerns were to prevent carbonization during the thermal treatments and to have an understanding of the relation between the gel preparation process and the removal processing of the organic groups.

Crystallinity of Gels

The primary concerns were to prepare gels without any crystallinity and to examine the crystallinity, if any, developed after the thermal treatments.

Gel Preparation Procedures

Several gel preparation procedures based on two different approaches have been developed.

The first approach consists of the reaction of all or most of the reactants in nonaqueous solvents. No deliberate initial partial hydrolysis of alkoxides was done. Initially, all or most of the reactants were allowed to mix and react with each other in a nonaqueous solvent. Subsequently,

the gelation was initiated by any one of the following ways: (a) adding
an aqueous solution of the water soluble reactant, (b) adding a limited
amount of water, (c) by exposing the final solution to atmospheric
moisture.

The second approach is based on the initial partial hydrolysis
of tetraethyl orthosilicate by the addition of a limited amount of water
and an acid catalyst before the addition of other constituents. Sub-
sequently, aqueous or nonaqueous solutions of the other constituents
are added for the reaction and gelation.

All procedures have been described below under two categories
based on the two approaches mentioned above.

The gel preparation procedures were developed using one compo-
sition. The composition of the batch are as follows:

$$SiO_2 \ 60, \ B_2O_3 \ 15, \ Na_2O \ 25 \text{ (weight percent)}$$

Procedures Based on First Approach

(1) **Procedure Ia**. The following starting chemicals were used
     as the source of different oxides:

Oxide	Source
SiO_2	Tetraethyl Orthosilicate
B_2O_3	Boric Acid dissolved in methanol
Na_2O	Sodium Carbonate

$Si(OC_2H_5)_4$ was mixed with about two thirds of its volume of
anhydrous ethanol in a round bottom flask with reflux con-
denser. The solution was stirred continuously. Then, boric
acid was dissolved in boiling methanol (~30 g/100 ml) and
poured into the ethyl orthosilicate solution. The solution
mixture was stirred for 1 hour at a temperature of ~50 C.
The pH of the solution was 6 . Then Na_2CO_3 dissolved
in water (~36 gm/100 ml) was added to the mixture with con-
stant stirring. The solution transformed into cloudy white
viscous colloidal solution. The pH changed to ~10. The

solution was stirred for 1/2-hour and was left overnight for
gelation. The sol converted into a gel on keeping overnight.
However, the gel was more like an opaque white mass rather
than translucent or transparent.

It should be noted that the addition of Na_2CO_3
causes instability in the solution containing the
reactants $Si(OC_2H_5)_4$ and boric acid. Hence, it is
anticipated that the homogeneity of the gel might
be good on a macroscopic scale, but the homogeneity
in a molecular state might not be good.

(2) **Procedure Ib**.

Starting Compounds: Tetraethyl Orthosilicate

Boric Acid

Sodium Nitrate

Tetraethyl orthosilicate was mixed with about the same
volume of anhydrous ethanol and was agitated for 5
minutes, then boric acid was dissolved in boiling
methanol (30 g/100 ml) and added to the solution.
The solution was stirred for 1/4 hour, then an aqueous
solution of $NaNO_3$ (57 percent) aqueous solution) was
added to the mixture. The solution became cloudy,
but on adding more water, it became clear. The con-
centration of $NaNO_3$ in water changed to 34 percent.
The gelation took place in 1-1/4 hours after the
addition of $NaNO_3$ solution.

(3) **Procedure Ic**.

Starting Compounds: Tetraethyl Orthosilicate

Boric Acid

Sodium Methylate

Tetraethyl orthosilicate was mixed with about 1/2 of its
volume of anhydrous ethanol. The boric acid dissolved
in boiling methanol (~30 g/100 ml was added to a solution
of tetraethyl orthosilicate. The solution was agitated
for 1 hour. The pH of the solution was about 6.00.
After 1 hour, $NaOCH_3$ in methanol solution (30 g/100 ml)
was added to the mixture. The pH increased to 9.2. The

solution was agitated for 3 hours. Water was added
drop by drop with continuous agitation of the solution.
The solution turned into a rigid gel on addition of
water. The amount of water added was 0.3 times the
theoretical water required for the complete hydrolysis
of tetraethysilicate.

In this procedure, all the constituents were in
the solution and were agitated for a significant
period of time for the homogeneous distribution of
cations.

(4) Procedure Id.

Starting Compounds: Tetraethyl Orthosilicate
                     Boric Acid
                     Sodium Methylate

This procedure was based on Procedure Ic (described above);
it differed in terms of amount of water for gelation.
The amount of water added in this case was 0.8 times the
theoretical water required for the complete hydrolysis
of tetraethyl orthosilicate, whereas in Procedure Ic this
value was 0.3.

(5) Procedure Ie.

Starting Compounds: Tetraethyl Orthosilicate
                     Boric Acid
                     Sodium Methylate

This procedure was also based on Procedure Id, but in this
case, the final solution was diluted with a mixture of water
and ethanol before gelation. The amount of water was the
same as it was with Procedure Id. The procedure was as
follows:

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Tetraethyl orthosilicate was mixed with an equal
volume of ethanol at approximately 40 C. The boric
acid dissolved in methanol was added. The resulting
mixture was stirred for 1 hour at approximately 40 C.
Then NaOCH$_3$ dissolved in methanol was added. The
mixture was stirred for 3 hours. The solution was
then mixed with a mixture of water and anhydrous
ethanol. The dilution was such that the concentration
of metal oxides in the solution became approximately
58 gms/lit. The amount of water was 0.8 times the
theoretical water required for the complete hydrolysis
of the tetraethyl orthosilicate. The final solution
was allowed to form gel. The viscosity of the solution
increased rapidly and a rigid gel was formed.

(6) Procedure If.

Starting Compounds: Tetraethyl Orthosilicate
                     Boric Acid
                     Sodium Methylate

This procedure was similar to Procedure Ie. In this case,
the dilution of the final solution was done with anhydrous
ethanol alone, no water was added. The dilution was such
that the concentration of oxide was about 40 gms/lit. The
solution was left at room temperature for gelation. A
transparent, rubbery gel formed after 2 hours.

Procedures Based on Second Approach

(1) Procedure IIa.

Starting Compounds: Tetraethyl Orthosilicate
                     Boric Acid
                     Sodium Methylate

The tetraethyl orthosilicate was mixed with an equal
volume of anhydrous ethanol. The solution was heated
up to approximately 40 C. Then a requisite amount
of water acidified with 1N HCl was added to the solution.
The amount of water was 0.14 times the theoretical
water required for the complete hydrolysis of tetraethyl
orthosilicate, and the concentration of HCl in the
resulting solution (i.e., the mixture of ethyl ortho-
silicate and ethanol) was about .04 gms/lit. The solution
was stirred for 5 minutes at approximately 40 C and was
cooled to room temperature. Then boric acid dissolved
in boiling methanol (33 gms/100 ml) was added. The
resulting mixture was stirred for 1 hour. After 1 hour,
the solution was acidified with acetic acid (anhydride).
The addition of acid was 5 ml per 100 ml of the resulting
solution. Then sodium methylate in methanol (10 gms/100 ml
of methanol) was added to the acidified solution with
constant agitation. The solution remained clear and stable
for about 2 minutes. Then a transparent rigid gel formed.

(2) Procedure IIb.

Starting Compounds: Tetraethyl Orthosilicate

Trimethyl Borate

Sodium Methylate

Tetraethyl orthosilicate was mixed with an equal volume
of anhydrous ethanol. The temperature of the solution
was raised to 40 C. Then a requisite amount of water
acidified with 1N HCl was added to the solution. The
amount of water was 0.26 times the theoretical water re-
quired for the complete hydrolysis of tetraethyl ortho-
silicate. After 45 minutes of stirring, trimethyl borate
was added to the solution. After 10 minutes, sodium
methylate in methanol (10 gms/100 ml) was added to the
solution and the solution was stirred for 45 minutes.
Finally, 20 ml of a mixture of water and ethanol (pro-
portion 1:4, by volume) was added to the solution. The

amount of water added at this stage was about 0.8 times
the theoretical water required for the complete hydrolysis
of the tetraethyl orthosilicates. The viscosity of
the solution increased rapidly and a rigid translucent
gel formed within 4 minutes after the addition of the
water alcohol mixture.

(3) Procedure IIc.

Starting Compounds: Tetraethyl Orthosilicate

Trimethyl Borate

Sodium Acetate

Tetraethyl orthosilicate was mixed with an equal volume of
anhydrous ethanol at 40 C. Then, a small amount of water
acidified with 1N 1 Cl was added to the solution. The
amount of water was 0.15 times the theoretical water
required for the complete hydrolysis of the tetraethyl
orthosilicate. The solution was agitated for 1/4 hour.
The solution was then cooled to room temperature and a
requisite amount of a trimethyl borate was added. The
solution was then agitated for 2-1/2 hours at room tempera-
ture. The pH was 6. Than an aqueous solution of sodium
acetate was added to the mixture. The concentration of
sodium acetate solution was about 1000 gms per liter.
The solution was acidified with acidic acid so that the pH
of the acetate solution was about 6. After the addition
of sodium acetate, the solution became slightly cloudy
and formed a translucent gel within 1/2 hour.

Thermal Treatment of Gels

The main objective of the thermal treatment is to remove the
volatile organic or inorganic compounds or groups (such as alcohols,

nitrates, hydroxyl groups, and alkoxy groups) by volatilization and de-
composition, and thus to transform the gel to homogeneous noncrystalline
oxides. After the preparation, the gel may be visualized as a system of
solid character in which the macromolecules are dispersed in a solvent
and somehow constitute a coherent structure. Thus, it contains the
solvent, the alcohols produced by the reaction, chemically bonded un-
reacted residual alkoxy groups and, residual unreacted water. Hence, the
following phenomena might occur during the thermal treatment:

- Removal of solvents and the release of free alcohols
  at lower temperatures
- Hydrolysis of the chemically bonded alkoxy groups
  with the atmospheric moisture or with the excess
  water incorporated during the preparation of gel
- Oxidation and removal of organic molecules as CO_2
  and H_2O at the later stage (<300 C) of thermal
  treatment. The presence of oxygen is beneficial
  at this stage.
- Formation of micropores with highly reactive surfaces
  after the removal of solvents and residual organic
  groups.
- Collapsing of pores to form a dense structure or
  to form closed pores.

The main concern for the thermal treatment in the present work is to de-
velop a procedure which would secure the maintenance of purity of the gel.
Hence, a long time consuming thermal treatment procedure is not desirable.
Thus, attempts were made to use a microwave oven at one step of the thermal
treatment procedure so that the time required for the thermal treatment
becomes short. Two thermal treatment procedures were used for the removal
of residual organic matters from the gels.

Thermal Treatment Procedure 1

This procedure was developed initially to investigate the removal process of organic matters. The procedure consisted of the following steps.

(1) Initial drying by an infrared heater (IR drying) for 2 days. The temperature was in the range of 60 to 80 C

(2) Microwave oven drying after IR drying. The period of microwave treatment was in the range of 9 to 12 minutes

(3) After the microwave oven treatment, samples were heated to 500 C in air. The rate of heating was about 150 C/hour and was held at 500 C for 2 hours.

Thermal Treatment Procedure 2

This procedure consists of heating in steps and a slow rate of heating. The procedure consists of the following steps after the initial drying of gels in air by the infrared heater:

(1) Drying in an air oven at ~80 C for 24 hours

(2) Heating at the rate of approximately 10 C/hour up to 150 C

(3) Holding at 150 C for 16 hours

(4) Heating from 150 C to 350 C at the rate of 10 C/hour

(5) Holding at 350 C for 8 hours

(6) Heating from 350 to 500 C at the rate of 10 C/hour

(7) Holding at 500 C for 12 hours.

The temperatures for holding were selected on the basis of the DTA results showing an endothermic peak around 150 C and an exothermic peak around 300 C. Most likely, the endothermic peak indicates the removal of absorbed water and alcohol and the exothermic peak indicates the burning of organic groups.

Effect of Humidity During Thermal Treatment

It was anticipated that the humidity during the thermal treatment would have a beneficial effect on the removal of residual organic groups. Hence, some preliminary investigations were done to see the effect of humidity treatment on the gels. Gel samples were treated at 66 C in a humidity chamber having a relative humidity of -76 percent. The humidity treatment of gels were done at different stages.

Effect of Aging or Storage of Gels

During the investigation on the removal of residual organic matter from the gels, it was observed that the aging or storage of gels at room temperature after certain stages of initial thermal treatment had an effect on the removal of the residual organic matters or groups.

After thermal treatment of the gels prepared by different methods, a visual comparison of the gel color was made. Results of the thermal treatments are shown in Table 2, and show the effects of humidity, heating rates, and preparation procedures.

Characterization of Gels

The following aspects of the physico-chemical nature of the gels were examined.

- Crystallinity by the X-ray diffraction powder pattern
- Molecular structure by the infrared spectroscopy.

TABLE 2.   THERMAL TREATMENT OF GELS

Preparation Procedure	Thermal Treatment	Gel Color	Comments
Ic	Procedure 1	Black to grey, became white when moistened with water during thermal treatment	Additional water during thermal treatment helps in the removal of organic groups
Ic	Humidity treatment of as-prepared gel fired to 500 C in air, held for 2 hours	White	Humidity treatment has a beneficial effect
Ic	As-prepared, IR dry, Microwave dry, humidity treated, fired to 500 C in air, held for 2 hours	Black to grey	Once the initial thermal treatment is done, humidity treatment has little effect
Id	Procedure 1	White	Addition of more water during gelation has a beneficial effect on the removal of residual organic groups
Id	Humidity treatment of as-prepared gel, fired to 500 C in air, held for 2 hours	White	Humidity treatment is beneficial
Id	Gel stored for 2 to 3 weeks after humidity treatment, fired to 500 C in air, held for 2 hours	Grey	It appears that aging at room temperature has an effect on the removal of organic groups

TABLE 2. (CONTINUED)

Preparation Procedure	Thermal Treatment	Gel Color	Comments
Id	Procedure 2	White	Slow heating rate and step heating are beneficial for the removal of organic groups
Ie	Procedure 2	"	—
If	Procedure 2	"	—
IIa	Procedure 1	Intense Black	Rapid heating rate is not desirable
IIa	Procedure 1	Brownish	Slow heating rate and step heating are beneficial
IIb	Procedure 1	White	Gel preparation procedure has an influence on the removal of organic groups
IIb	Procedure 2	"	"

Crystallinity

X-ray diffraction powder patterns of as-prepared and the gels after different stages of thermal treatment were taken. The results are shown in Table 3, and describe the effects of preparation procedures and thermal treatment on crystallinity.

Molecular Structure

Infrared spectroscopy was used to get some ideas about the molecular structures of the "as prepared" gels and of the gels obtained after various thermal treatments. The infrared spectra of gel powders were taken using the KBr briquette technique. The complete spectrum from 400 to 3600 cm^{-1} was taken.

The characteristic features of the spectra obtained with the gels prepared by the different procedures were compared. The effect of thermal treatment on the positions of the absorption bands was investigated. The change in intensities of the absorption peaks were observed qualitatively.

The absorption band at around 1000 cm^{-1} results from vibrations involving the largest force constant due to Si-O bond stretching. The position and features of thi absorption peak obtained with gels prepared by the different powders were compared. The provisional assignments of different absorption bands in the region 3600 to 400 cm^{-1} are given in Table 4. The infrared spectra of different gels which were not subjected to any thermal treatment are shown in Figures 5 to 8. The results of the comparison of the position and features of the absorption band due to Si-O-Si stretching obtained with different gels are summarized in Table 5. It is evident from the figures and also from Table 4 that the positions and characteristic features of the absorption bands obtained with different gels are not the same. It should also be noted that the intensity of a weaker band at 800 cm^{-1} is also not the same in all cases. The effects of the following thermal treatments were examined qualitatively.

TABLE 3.   CRYSTALLINITY OF GELS

Preparation Procedure	Thermal Treatment	Crystallinity
Ib	As prepared	Crystallinity due to $NaNO_3$
Ib	After infrared drying	"
Ib	After IR drying and Microwave drying	"
Ib	After IR drying, Microwave drying and 2 hours at 350 C	Crystallinity due to $NaNO_3$ but much less than as prepared gel
Ic	As prepared, and drying	Noncrystalline
Ic	After Microwave drying	"
Ic	After IR drying, Microwave drying and 350 C for 2 hours	"
Id	After thermal treatment at 500 C for 12 hours (thermal treatment Procedure 2)	"

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As Prepared Gel: Procedure Ib

As Prepared Gel: Procedure Id
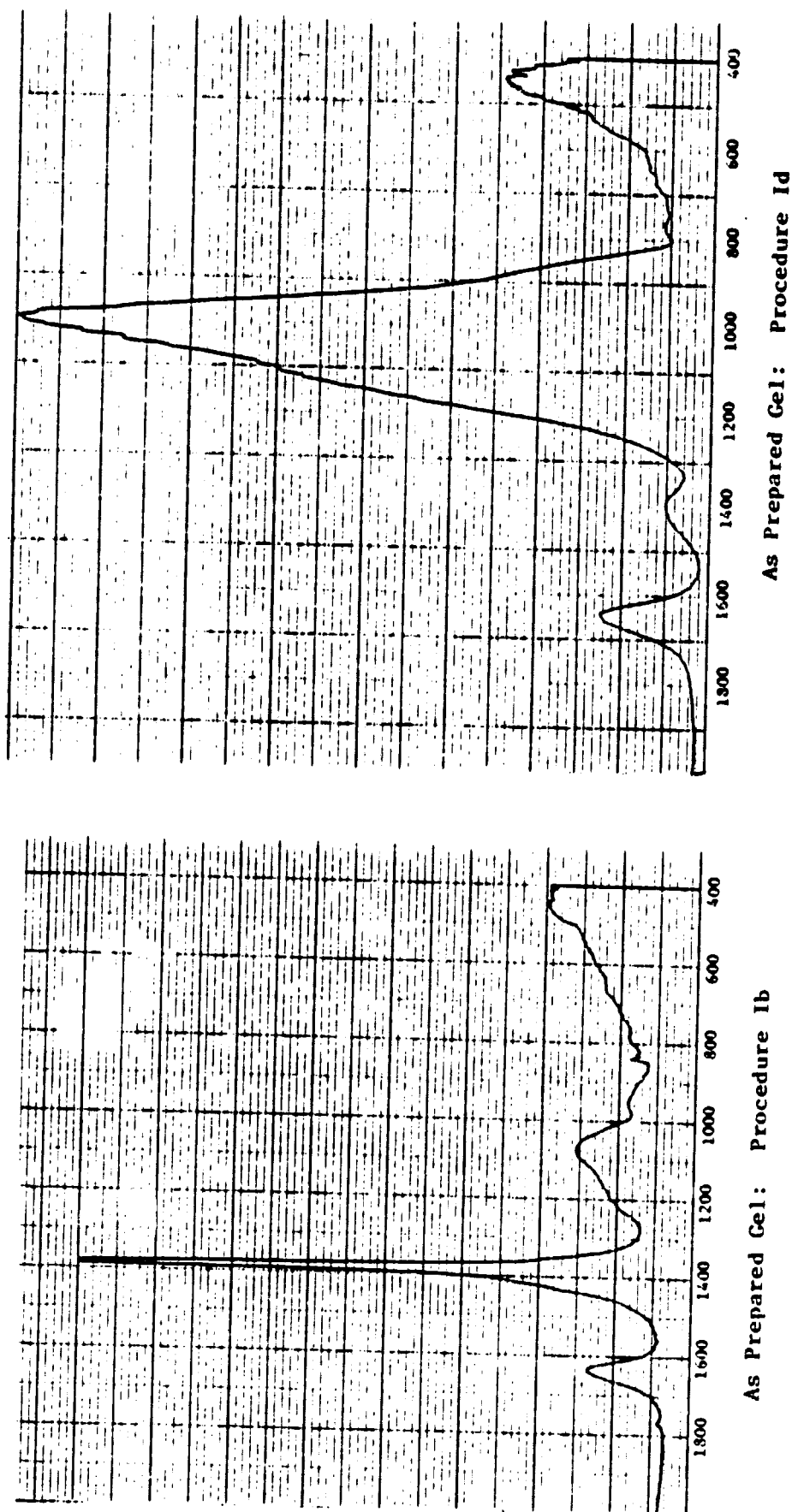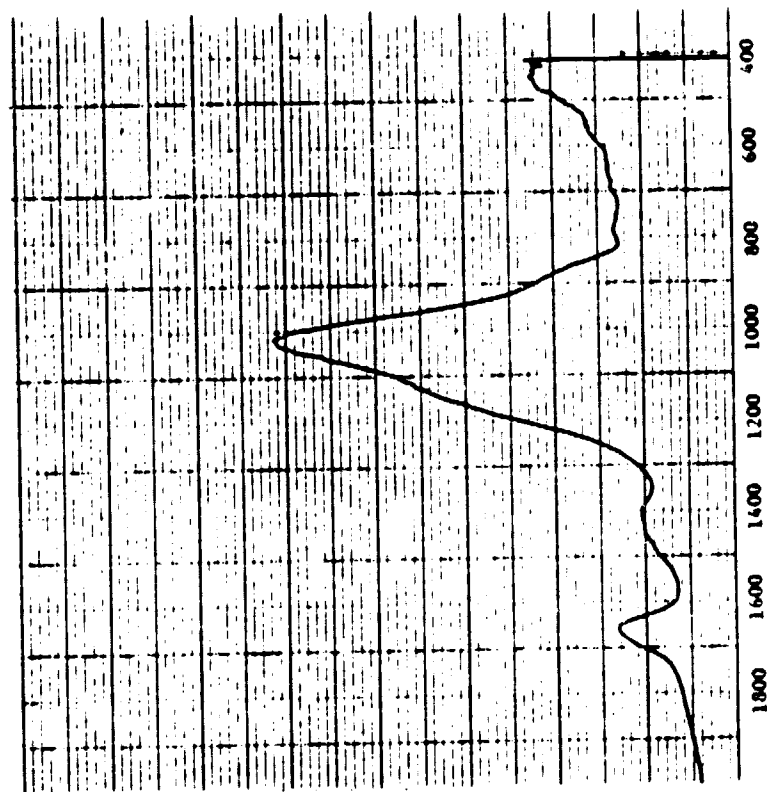
FIGURE 5. INFRARED SPECTRA OF GELS PREPARED BY PROCEDURES Ib AND Id

As Prepared Gel: Procedure If

FIGURE 6. INFRARED SPECTRA OF GELS PREPARED BY PROCEDURE I f
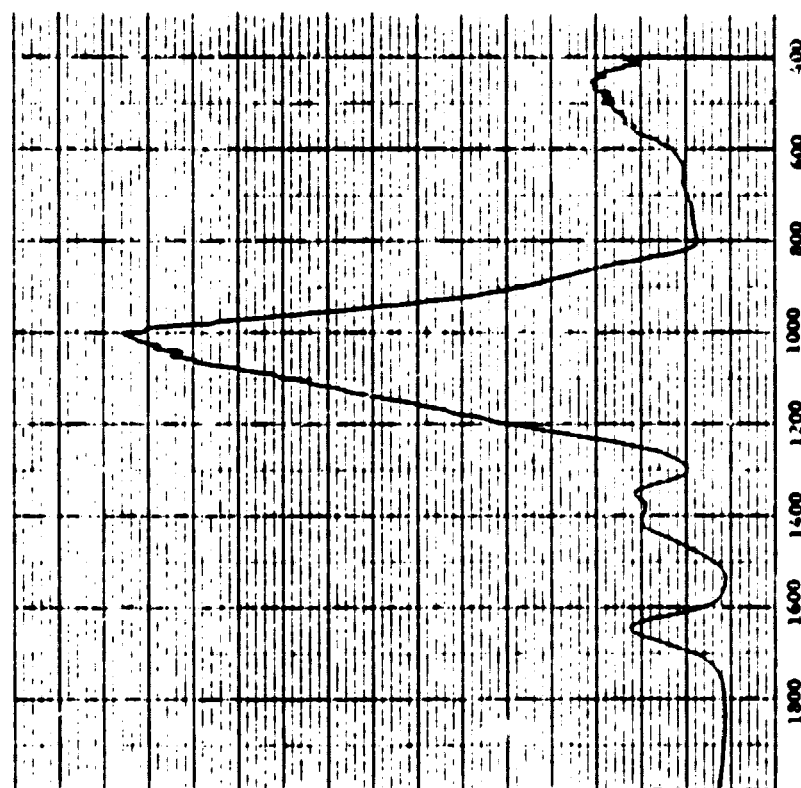
As Prepared Gel: Procedure IIb
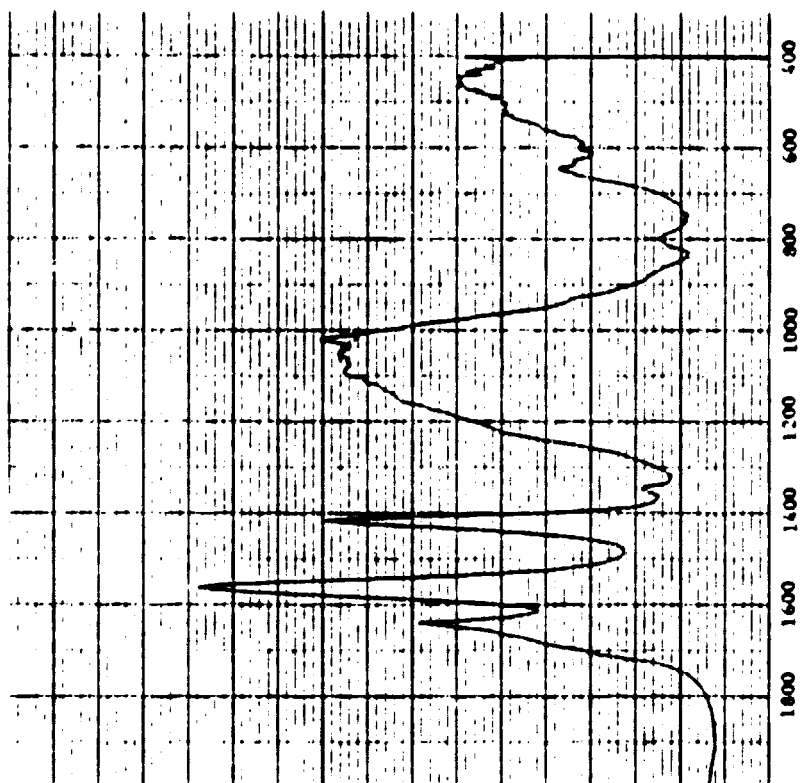
As Prepared Gel: Procedure IIa

FIGURE 7. INFRARED SPECTRA OF GELS PREPARED BY PROCEDURE IIa, IIb
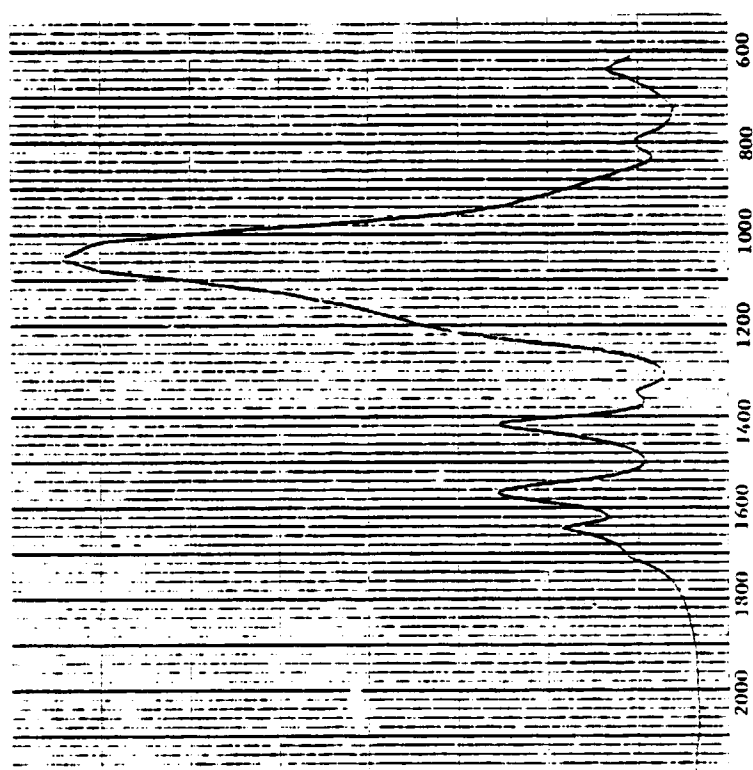
As Prepared Gel: Procedure IIc

FIGURE 8.   INFRARED SPECTRA OF GEL PREPARED BY PROCEDURE IIc

TABLE 4. INFRARED ABSORPTION BANDS AND THEIR
PROVISIONAL ASSIGNMENT

Absorption Band $(\nu)\ cm^{-1}$	Provisional Agreement
3600 - 3200	Combined as well as absorbed water
3200 - 3100	OH^- groups in alcohols
2900 - 2800	CH stretching frequencies CH_3, CH_2 , CH
1600 - 1680	Free H_2O
1275 - 1470	CH deformation frequencies
1160 - 1100	Si-O C_2H_5
1020 - 1090	Stretching Si-O-Si, Si-O-C
960 - 950	Si-O-C_2H_5 Si-O-B Si-OH
800	Si-O-Si

TABLE 5. CHARACTERISTICS OF THE IR ABSORPTION
BANDS (DUE TO Si-O STRETCHING) OF
DIFFERENT GELS

Gel Preparation Procedure	Thermal Treatment	Absorption Band (Wave Number (cm^{-1})
Ib	As prepared	1080 (Broad half-width with a weak shoulder at $1200\ cm^{-1}$)
Ic Id	"	1000 (Sharp peak, with narrow half-width)
Ie If	"	1020-1030 (Sharp peak, the features are similar to those of gel Ic and Id)
IIa	"	1080-1030 (broad peak, and broad half-width)
IIb	"	1000 (Sharp peak)
IIc	"	1060 (Sharp peak, with a very weak shoulder at $1200\ cm^{-1}$)

- Infrared heater drying
- Microwave oven drying
- Humidity treatment
- Heat treatment up to 500 C.

The results showed that the positions of the absorption bands of "as prepared" gels did not shift after any one of the above thermal treatment steps. The major change was in the intensity of the band due to CH_3 or CH_2 groups and hydroxyl groups. The infrared spectra of the gels after thermal treatment up to 500 C are illustrated in Figures 9 and 10. Because the spectrum was taken using the KBr briquette technique, the proper monitoring of the bands due to hydroxyl groups was not possible. It was observed qualitatively that the intensity of the band due to CH_3 or CH_2 groups reduced slightly after microwave treatments. The thermal treatment up to 500 C with a very slow rate of heating and step heating made considerable reduction of organic groups. However, interesting results were obtained with the gels after humidity treatment. It appeared that humidity treatment had a marked effect on the removal of organic groups. After humidity treatment this peak remained in the same position, but the half-width became broader. It appears that polymerization as well as the release of organic groups as vapor occur during the humidity treatment. The intensities of the absorption bands in the region 2800 to 3600 cm^{-1} decreased with increase of thermal treatment. But, the presence of a weak absorption band at ~1400 cm^{-1} due to -CH- deformation was observed even with the white color gels obtained after the thermal treatment at 500 C.

Melting of Gels

The gels, after initial thermal treatment, were melted at different temperatures for different periods. The object was to investigate the nature of glass in terms of carbon retention. The color and transparency of the glass were observed after each melting. The melting was done in an air atmosphere in an alumina crucible or in a platinum boat. The results obtained with gels prepared by Procedure Id are shown in Table 6.
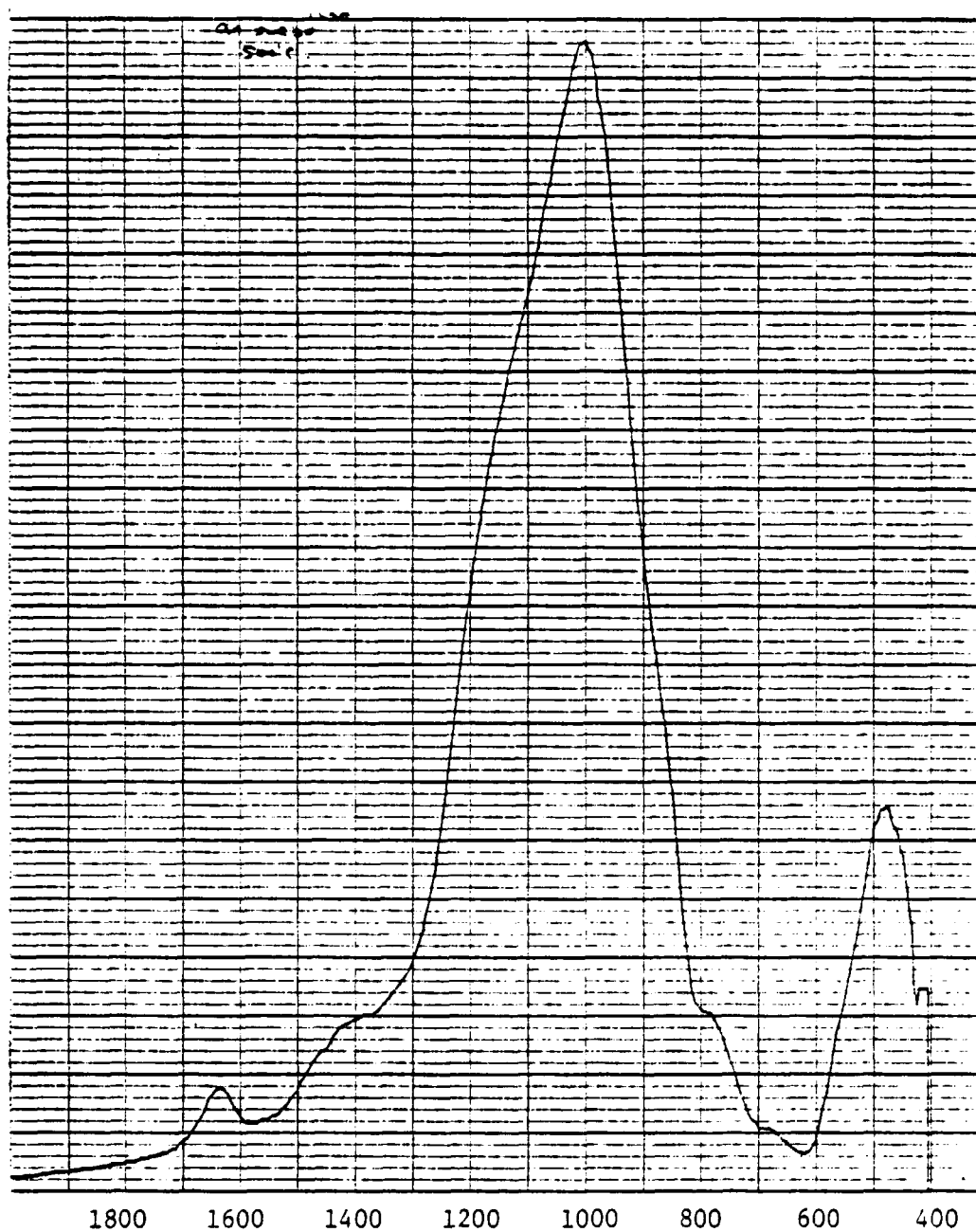
FIGURE 9. INFRARED SPECTRA OF GELS PREPARED BY PROCEDURE
Id AFTER THERMAL TREATMENT UP TO 500 C
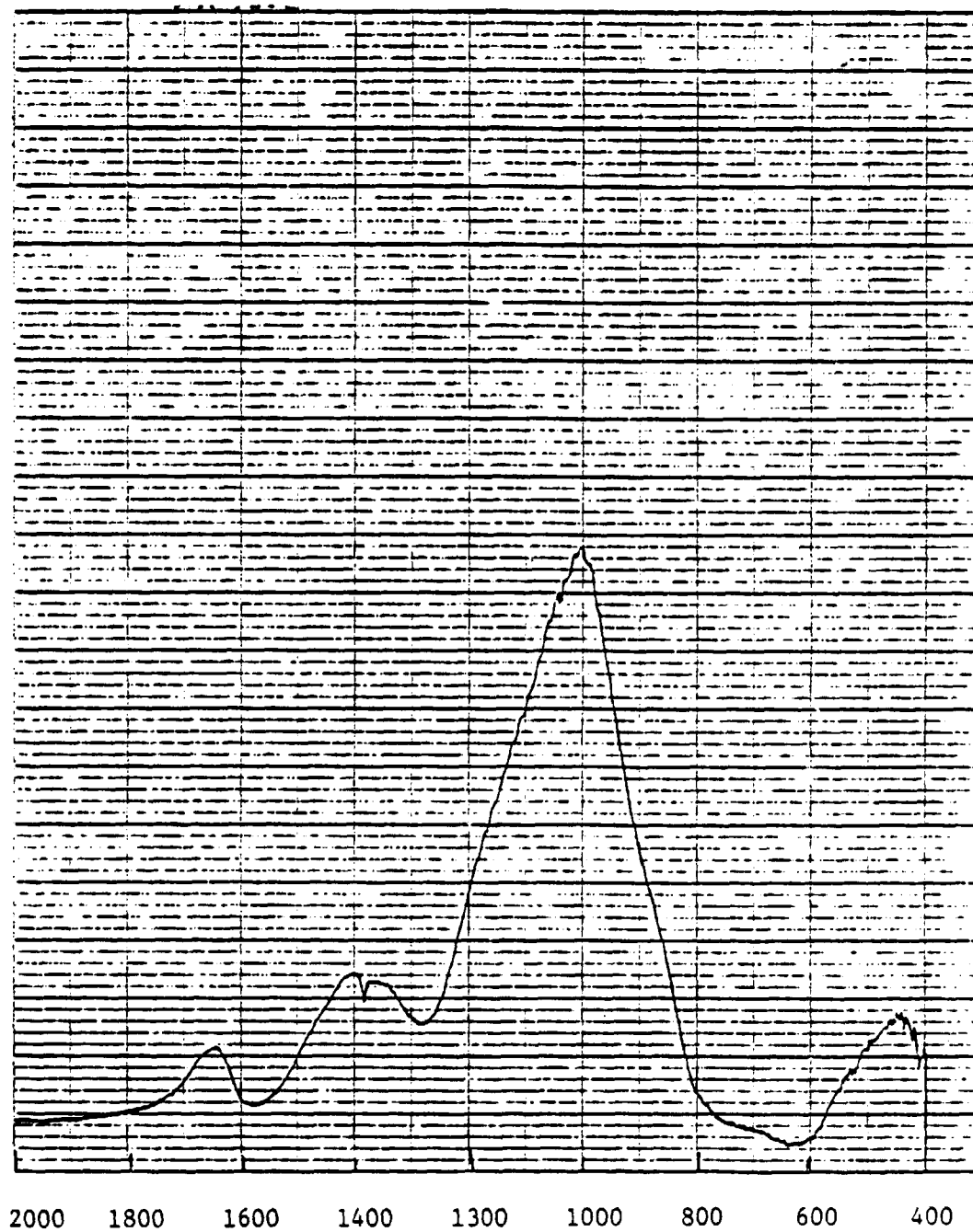
FIGURE 10. INFRARED SPECTRA OF GELS PREPARED BY
PROCEDURE IIb AFTER THERMAL TREATMENT
UP TO 500 C

TABLE 6. EFFECT OF TIME AND TEMPERATURE ON THE MELTING OF GELS
(APPROXIMATELY 5 gm SAMPLE) PREPARED BY PROCEDURE Id

Experiment Number	Thermal Treatment	Melting Temperature	Melting Time (hour)	Results
1	After Infrared heater drying	1000 C	1	Grey color but transparent, numerous bubbles
2	"	"	2	Much less grey, transparent, numerous bubbles
3	"	"	3	Colorless and transparent, less bubbles
4	"	"	4	Colorless and transparent, much less bubbles
5	"	"	5	Highly transparent, bubbles undetected
6	"	1100 C	1	Grey, but much less than that of Experiment 1
7	"	"	2	Quite transparent and colorless, no detectable bubbles
8	"	"	3	Highly transparent, colorless, no bubbles
9	"	"	4	"
10	"	"	5	"
11	"	1200 C	1	Highly transparent, colorless, and no bubbles
12	"	"	2	"

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DISCUSSION

Preparation of Gels

The formation of silica gels from alkoxysilane is primarily based on the hydrolytic polycondensation of alkoxysilane. The overall reaction can be represented as follows:

$$n \ Si \ (OC_2H_5)_4 + 4n \ H_2O$$

$$\longrightarrow n \ Si(OH)_4 + 4n \ C_2H_5OH$$

$$n \ Si(OH)_4 \longrightarrow (SiO_2)_n + 2n \ H_2O$$

$$(Gel)$$
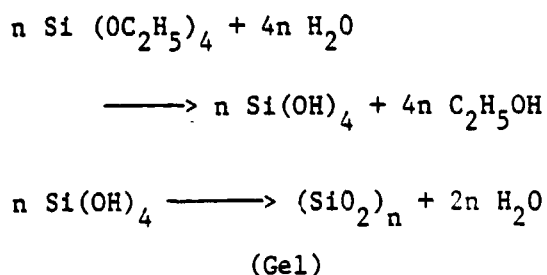
The mechanism of hydrolysis and polycondensation of tetraethyl orthosilicate has been studied by Aelion, et al[16]. The hydrolysis is strongly catalyzed both by acids and by bases. It is reported[16] that the kinetics of acid hydrolysis is a second order reaction with respect to water and ethyl silicate. It is supposed that hydronium ion attacks the polar $\equiv SiO \ C_2H_5$ band and forms $\equiv Si\text{-}OH$ groups.

$$\equiv SiO \ C_2H_5 + H_2O + HCl \longrightarrow \ \equiv Si \ OH$$

$$+ \ C_2H_5 \ OH + HCl.$$
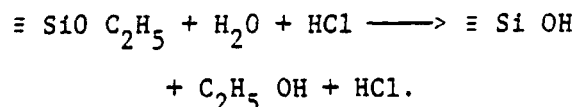
Subsequently, $\equiv Si \ OH$ groups undergo polycondensation reaction to form siloxane ($\equiv Si\text{-}O\text{-}Si \equiv$) bonds, and polymerization proceeds.

In strongly acid solutions, where the hydrolysis reaction is rapid, the polymer remains in the solution and the rate of gelation is low. The polymeric species contain less number of unreacted ethoxy groups, but hydroxyl groups remain with polymeric species.

The mechanism of alkaline hydrolysis involves coordination of OH^- to silicon followed by rejection of an alkoxide ion:

$$\equiv \text{Si OC}_2\text{H}_5 + \text{OH}^- \longrightarrow \quad \equiv \overset{\cdot\cdot}{\underset{\underset{H}{O}}{\text{Si}}} - \text{OC}_2\text{H}_5$$

$$\Big\downarrow$$

$$\equiv \text{Si OH} + \overline{O}\ \text{C}_2\text{H}_5$$

$$\overline{O}\ \text{C}_2\text{H}_5 + \text{H}_2\text{O} \longrightarrow \text{C}_2\text{H}_5\text{OH} + \text{OH}^-$$
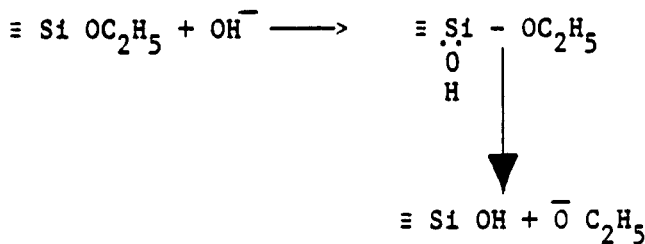
Subsequently $\equiv$ Si OH groups condense to form siloxane bonds.

The expanded coordination shell for silicon is postulated and pentacoordinated intermediates of this short have been established with considerable certainty in many reactions involving organosilicon reactions.
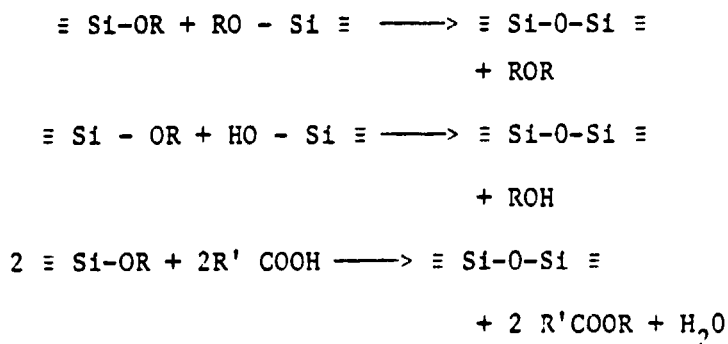
In the basic solution, the hydrolysis is first order with respect to ethyl silicate. The condensation of $\equiv$ Si OH groups takes place more rapidly in alkaline solutions than in acid solutions.

It should be noted that the rate of hydrolysis depends significantly on the size of the alkyl groups in the ester. Methyl and ethyl esters are most susceptable to hydrolysis. The rate of hydrolysis falls with the increasing number of carbon atoms and with the increasing branching of the hydrocarbon groups. The bulkiness of the structure of the alkoxy groups and consequently, a steric screening of the Si-OC bond increases the resistance to hydrolysis.

However, in the absence of water, some nonhydrolytic processes for the formation of Si-O-Si bonds form alkoxysilanes could take place. The relevant reactions relevant to the present work are as follows:

$$\equiv \text{Si-OR} + \text{RO} - \text{Si} \equiv \longrightarrow \equiv \text{Si-O-Si} \equiv$$
$$+ \text{ROR}$$

$$\equiv \text{Si} - \text{OR} + \text{HO} - \text{Si} \equiv \longrightarrow \equiv \text{Si-O-Si} \equiv$$
$$+ \text{ROH}$$

$$2 \equiv \text{Si-OR} + 2\text{R}' \text{COOH} \longrightarrow \equiv \text{Si-O-Si} \equiv$$
$$+ 2\ \text{R}'\text{COOR} + \text{H}_2\text{O}$$

The picture of the gelling process given above is a simple gelling process of the alkoxysilane itself. The process becomes more complicated in a multicomponent system containing both network forming constituents like B_2O_3 and a network modifier like Na_2O. However, it is anticipated that the basic reaction processes will be similar, but the kinetics of the process will change because of the catalytic action and the change of pH due to the presence of other reactants.

The formation of borosiloxane bonds $\equiv Si-O-B \equiv$ in the present systems can take place as follows:

- The reaction of boric acid with alkoxysilanes:

$$\equiv B-OH + R \ O-Si \ \equiv$$

$$\longrightarrow \ \equiv B-O-Si \equiv + \ ROH$$
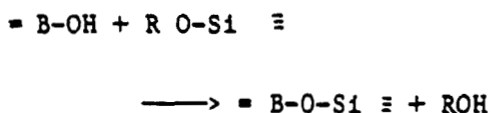
- The reaction of boric acid with silanols:

$$\equiv BOH + HO-Si \equiv \longrightarrow \equiv B-O-Si \equiv$$
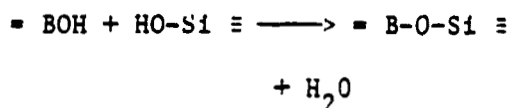
$$+ \ H_2O$$

- The reaction of boric esters with silanols:

$$\equiv B-OR + HO-Si \equiv \longrightarrow \equiv Si-O-B \equiv$$
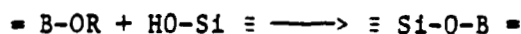
- The reaction of boric esters with alkoxy silane:

$$\equiv B-OR + RO-Si \equiv \longrightarrow \equiv B-O-Si \equiv$$
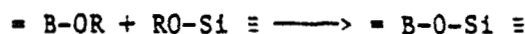
The incorporation of Na^+ ion into the gel structures could take place as follows:

$$\equiv Si-OR + NaOH \longrightarrow \equiv Si-ONa + ROH$$

(from the hydrolysis of sodium
   methylate sodium acetate)

$$\equiv Si-OH + Na^+ \xrightarrow[\text{exchange}]{\text{ion}} \equiv Si-O \ Na^+$$
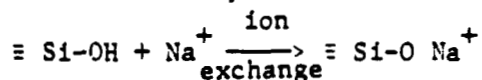
(from aqueous solution of
   $NaNO_3$ or NaAc)

Hence, it may be stated that the important parameters that control the gelling process are as follows:

- Chemical nature of the starting compounds
- Concentration of water
- Presence of a catalyst
- pH of the medium
- Concentration of the reactants and
  the solvents used.

Several procedures based on two different approaches have been developed for the preparation of gels. The first approach leads to the preparation of a stable, clear solution which is highly homogeneous and may be partially polymerized. Subsequently, the solution is polymerized or gelled in the presence of added water or atmospheric moisture. Because the solution contains insufficient water, there are some difficulties with this approach in achieving effective hydrolysis and subsequent removal of alkoxy groups during thermal treatment. However, it should be noted that this problem can be avoided by taking appropriate measures, such as the addition of reactive water molecules, and the dilution of the solution with anhydrous ethanol. The use of an aqueous solution of sodium nitrate as a source of Na_2O causes the segregation of sodium nitrate in the aqueous phase. If the amount of water is sufficiently high, sodium nitrate remains in an aqueous solution and a clear solution as well as a clear gel is obtained. Subsequently, some of the sodium ions are incorporated into the gel structures, but a portion of the sodium nitrate remains as sodium nitrate, and the removal of water during the initial thermal treatment causes the precipitation of sodium nitrate. This is evident from the results of the X-ray diffraction studies.

When an aqueous solution of Na_2CO_3 is used as the source of Na_2O, the formation of colloidal silica/silicates takes place. This is due to the polycondensation of $\equiv SiOH$ groups which is very rapid in alkaline medium.

Several approaches for the preparation of gels, based on the second approach involving initial partial hydrolysis of tetraethyl orthosilicate, have been developed. The results suggest that the main concern in this approach is to maintain the stability of the solution on addition of sodium methylate, which is highly reactive to water and causes a sharp

rise of pH in the solution and thus enhances the gelation. The use of an
aqueous solution of sodium acetate instead of sodium methylate reduces this
problem to a considerable extent. The results indicate that a stable, clear
solution can be prepared by the proper control of pH and water concentration.
It is anticipated that the initial hydrolysis of tetraethyl orthosilicate
and the presence of excess water in the solution are beneficial for the
removal of the alkoxy groups.

Thermal Treatment of Gels

The "as prepared" gels may be considered as a system of solid
character in which macromolecules are dispersed in a solvent and somehow
constitute a coherent structure. Thus, it contains the structural skeleton
of the silicate network; unreacted alkoxy groups chemically bonded to
the silicate network; free solvents, like alcohols and water; and alcohols
and water adsorbed to the silicate structures. Hence, the removal of
these organic compounds and also inorganic radicals, such as nitrates, is a
complex phenomenon and is related to the structure and morphology of the
gels which in turn is related to the gel preparation procedures. The results of
the present work suggest that the gel preparation procedure has an in-
fluence on the removal of organic groups during the thermal treatment. The
results showed that if the residual organic groups are not removed during
the low temperature thermal treatments (e.g., <500 C), the pyrolysis of
the organic group occurs at high temperatures and elemental carbon forms.
This was evident from the grey to black color of the gel. The results of
the present work indicate that the following factors in the gel preparation
process are important for the removal of organic groups during the thermal
treatments.

- An additional incorporation of active water molecules
  during gelation has a beneficial effect on the removal
  of organic groups
- The thermal treatment of gels in a humidity chamber
  (80 percent RH, 66 C) just after preparation has
  a marked beneficial effect on the removal of organic
  groups. This suggests that the hydrolysis and increased
  polymerization can take place in the solid phase. The

water vapor reacts with the unreacted ethoxy groups during the humidity treatment and causes further polycondensation

- The critical partial hydrolysis of tetraethyl orthosilicate in the presence of an acid catalyst is also helpful in the removal of organic groups

- The aging of gel on storage after initial drying by the infrared heater or microwave oven has an adverse effect on the removal of organic groups. The exact reason for this is not well understood. It is anticipated that this could be due to the hydrolytic polycondensation during aging which may reduce the reactivity of atmospheric moisture with the gel particles

- The dilution of the final solution with anhydrous alcohol has a marked beneficial effect on the removal of organic groups.

The results of the effect of different thermal treatment procedures indicate that thermal treatments involving heating in steps and a slow rate of heating are most desirable for the removal of residual organic groups. It is anticipated that these steps are most likely related to different reactions that take place at different temperatures. The presence of an endothermic peak at around 150 C and an exothermic peak around 300 C in the DTA curve might be correlated with the evaporation of solvents and the oxidation of organic groups, respectively. It should be noted, however, that the kind of thermal treatment procedure required for the removal of organic groups depends on the gel preparation procedure and the composition of the gel.

Structural Characterization

Infrared spectroscopic studies of the gels prepared by the different procedures throw some light on the molecular structures of the gels prepared by the different procedures. It is evident from Figures 5 to 8 and Table 5 that the position and features of the absorption band due to Si-O bond stretching are not the same in all the gels prepared by the different preparation procedures.

The peak positions of absorption bands obtained with the gels prepared by Procedures Ic, Id, Ie, If and IIb are in the region 1000 to 1030 cm^{-1}.

The peak positions of the absorption bands obtained with the gels prepared by Procedures Ib, IIa and IIc are in the region 1080 to 1030 cm^{-1}. It was also observed that this position did not shift by any thermal treatment steps up to 500 C. The humidity treatment of the gels did not cause any shift of the peak position. It was mentioned earlier that the humidity treatment had an effect on the hydrolysis of unreacted ethoxy groups chemically bonded to silicon-oxygen skeleton. Thus, it is assumed that these differences in the positions and the features of the absorption bands might be due to the difference in the polymeric structures of the gels.

In vitreous silica, the absorption band due to Si-O-Si bond stretching is at 1100 cm^{-1}. The Si-O stretching vibration compounds containing Si-O linkage gives rise to the absorption band in the region 1010 cm^{-1} to 1090 cm^{-1}. But, the position of the peak depends on the nature of the polymers. There are some differences between cyclic and open-chain compounds; in the case of cyclic compounds, the position of absorption peak shifts with increased ring size. It has been reported[17] that in the trimer the Si-O band appears at 1018 cm^{-1} while still in the higher ring it falls in the range of 1076 to 1056 cm^{-1}, the frequency showing a small but steady fall with increase of ring size from three to eight. It has also been reported[18] that there was remarkably little difference in the position of the Si-O-Si absorption bands with variations in the nature of substituents (e.g., SiR R$_2$O) although there was a considerable shift between trimers and tetramers. The Si-O absorption band in the open chain polymeric siloxanes lies in the range of 1055 to 1024 cm^{-1} and again, there is a small fall in the frequency for each unit increase of the chain length. [17]

Hence, most likely, the difference in the peak positions are due to the structural difference in the polymer, the nature of which is controlled by the preparation procedures. The present experimental results are not sufficient enough to identify the main parameter(s) in the preparation process which is controlling the structure of the polymer. However, it has been observed that significant changes (in the preparation procedure) are to be made to get an appreciable change in the shift of the absorption peak. It

should be noted that a systematic investigation involving precise control of the process parameters and the structural investigations of the gels thus prepared may clarify the structural aspects speculated above.

Melting of Gels

The gels used for the melting studies were taken from materials that had only been IR heater dried; consequently, a considerable amount of organic compounds were incorporated with the gels. Moreover, the gel powders were not slowly heated up to the melting temperatures. The objective was to investigate the effect of temperature and time on the elimination of carbon. It is evident from the results shown in Table 6 that the elimination of carbon during melting of the glass in an air atmosphere is a function of time and temperature. The time required to eliminate carbon and bubbles (with a 5 gm batch) is 5 hours at 1000 C, and it reduced to 1 hour at 1200 C. Hence, it is anticipated that the time and temperature of melting will be reduced considerably with gels having thermal treatments up to 500 C. However, the main concern at the melting stage is to know the influence of melting history on the molecular structure of the glass and the redox state of the glass.

CONCLUSIONS

The alkali-borosilicate system has been selected as the glass system for the preparation of ultrapure low loss glasses suitable for optical communication. The effect of different oxide contents (e.g., B_2O_3, Na_2O) on the absorption loss has been critically reviewed. At present, one composition has been chosen to develop the gel preparation procedure in the alkali-borosilicate system. In addition, several approaches for the preparation of gels based on two different approaches have been developed, and the influence of different gel preparation parameters (such as pH, water concentration, and starting compounds) have been investigated qualitatively.

Several conclusions can be drawn from the results of the initial activities of the present research program, and they are as follows:

- Gels produced are noncrystalline and remain so after thermal treatment at 500 C

- The residual organic compounds in the gels can be removed by the appropriate thermal treatments up to 500 C.

- The removal of organic groups during low temperature thermal treatments is related to gel preparation, ambient atmosphere (e.g., humidity) and the thermal treatment procedure.

- The infrared spectra of the gels suggests that the main characteristic structural features of the gel prepared by different procedures are similar, but there exists some finer structural differences as revealed by the spectra·

- The rate of removal of carbon from the glass during the melting of gels containing a major proportion of residual organic compounds is a function of temperature. A colorless transparent glass from a particular gel was obtained by melting at 1000 C for 3 hours, whereas the time reduced to 1 hour when the melting temperature was 1200 C. Hence, it is anticipated that the time and temperature of melting will be reduced considerably with gels having no or minimum residual organic groups.

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